Comparison of Polyurethane Foam-Based Passive Air Samplers: Single vs Double Disk

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Abstract

To aid in the detection of trace-level atmospheric pollutants, a field study was undertaken using polyurethane foam (PUF) based passive air samplers, looking at increasing the sampling phase from one to two PUF disks per deployment chamber. The use of the two PUF disks configuration would increase both the volume and surface area of the sampling phase and therefore may aid in the detection of compounds present at trace to ultra-trace levels. However the addition of the extra PUF may alter the uptake kinetics of the sampler and this study was undertaken to assess these potential alterations. Sixteen PAHs, which have previously been shown to be present in Brisbane air at low levels, were monitored at one site in Brisbane using both sampler configurations deployed for up to 40 days. For all PAHs, the quantities accumulated in the 2-PUF samplers were greater than in the 1-PUF samplers, as would be expected from passive sampler theory. On average the difference in accumulation was a factor of 1.8. Performance reference compounds were lost at almost identical rates from both 1 & 2-PUF samplers, indicating the models currently used to describe sampling rates and atmospheric concentrations are still applicable to the new design.

Introduction

Recent work by Lim et al (2005)[1] has shown PAHs to be present in the Brisbane atmosphere at low concentrations; however the potent carcinogenicity of certain PAH means there may be no safe threshold value for exposure to these. In order to be able to quantify these trace-level compounds without the use of resource intensive high-volume sampling, investigations were made into practical means of passive sampling over relatively short periods of time (≈ month).

Passive sampler theory has been discussed in a number of publications [2]. Equation 1 describes the change of sampler concentrations with time which is effectively uptake minus loss.

$$dC_s/dt = (k_O*(A_s/V_s))*C_v - (k_O*(A_s/K_{sv}*V_s))*C_s \qquad [1]$$

Where k_O is the overall mass transfer coefficient, K_{SV} is the sampler-air partition coefficient, C_A and C_S are the concentration in the ambient air and the sampler respectively and A_S and V_S are sampler surface area and volume respectively. While sampling remains time integrated (linear phase), loss rates are negligible due to the relatively large K_{sv} of most PAHs, until C_s becomes significant and equilibrium is approached. During the linear phase, assuming C_A to be constant, equation 1 can be simplified, then integrated to give an equation based on mass of analyte in sampler (N_s):

$$N_s = A_s k_o C_v\, t \qquad [2]$$

At equilibrium, equation 1 can be rearranged and integrated to give:

$$N_s\ (eq) = K_{sv} C_v V_s \qquad [3]$$

These equations show that during the initial, linear stages of uptake, sequestered masses will be proportional to the samplers' surface area, and at equilibrium, proportional to the samplers' volume. Therefore by using two PUF disks rather than one, we should be find an increase in sampler concentrations for compounds both at equilibrium and in the kinetic phase. However the presence of the second PUF may influence the nature of airflow within the chamber, and this in turn must have some influence on the uptake kinetics of the sampler as a whole. Airflow within a single PUF chamber has been modeled using computational fluid dynamics, and a stagnant area of recirculation was predicted above the disk[3]. The presence of the second disk in our experimental configuration (see Figure 1) could potentially result in a relatively stagnant layer between the two disks possibly slowing uptake, due to an increase in boundary layer thickness or a lessening of effective surface area.

Samplers may be loaded with performance reference compounds (PRCs) before deployment to confirm uptake kinetics. The loss rate constant for PRCs from the sampler is assumed to be analogous to uptake of analytes[4]. If the loss rates from both the 1- and 2-PUF configurations are the same then the addition of the seond PUF disk is not influencing uptake kinetics. Therefore if a doubling of amounts accumulated is observed whilst loss rates remain constant between both the 1- and 2-PUF configurations we may confirm that the uptake kinetics have not been influenced by the addition of the second PUF. PRC loss rate constants (k_e), may be calculated as follows:

$$k_e = (\ln(C_0/C))/t \qquad [4]$$

Where C is the PRC concentration in the sampler after t days, and C_0 the initial sampler PRC concentration.

Materials and Methods

The passive samplers consisted of one or two PUF discs held in bowl chambers which have been previously characterized[5]. Details of the configuration of the PUF within the chambers may be seen in Figure 1. Three single PUF samplers (1-PUF) and three double PUF samplers (2-PUF) were deployed for up to 40 days at one site in Brisbane, Australia. The passive samplers were deployed close to the Brisbane CBD near a 6 lane motorway during summer, from December 2006 to January 2007.

(1a) (1b)

Figure 1: PUF disks housed in passive sampling chamber with both 1-PUF (1a) and 2-PUF (1b) configurations.

All PUF was pre-extracted on an accelerated solvent extractor (ASE) (Dionex ASE300) using dichloromethane as the solvent. Before deployment, passive samplers were loaded following the method used by Wilford *et al.*[6] with a mixture of PCBs and deuterated PAHs (PCB #'s 14, 21, 30, 204 and *d10*-Anthracene and *d10*-Pyrene) to act as performance reference compounds (PRCs). Post deployment samples were extracted on the ASE following the same method used for pre-extraction. Extracts from both disks in the 2-PUF samplers were combined to give one sample. Samples were concentrated by evaporation and cleaned by gel permeation chromatography (GPC) to remove high molecular weight potential interferences (for further GPC details see Bartkow *et al.*[7]). The samples were solvent exchanged into ethyl acetate before analysis on the GC/MS. GC/MS was operated in SIM mode (Column ZB-1 ms, length 25m, diameter 0.2mm, film thickness 0.33µm, carrier gas He. Injection vaporisation temperature: 250°C, Program 65°C for 2 min, ramp 20°C/min to 295°C hold 10.6 min). The US EPA 'priority 16' PAHs were quantified using internal standards added to the samplers prior to extraction. Recoveries ranged from 83 to 170 %

Results and Discussion

Masses of the targets accumulated in both configurations of the passive samplers are presented in Table 1, along with averages and standard deviations. Also shown are the ratios of the masses accumulated in the 2-PUF and 1-PUF disk configurations. Table 2 shows the PRC elimination rate constants for both configurations.

Table 1: Masses of PAHs accumulated in passive samplers after 40 days

	1-PUF		2-PUF		Ratio of
	Average (ng)	Standard	Average (ng)	Standard	Averages
PAH	*n=3*	Deviation	*n=3*	Deviation	(2/1)
Naphthalene	54.0	16.1	82.4	7.7	**1.5**
Acenaphthylene	7.2	0.6	13.8	1.6	**1.9**
Acenaphthene	3.7	0.8	5.2	5.1	**1.4**
Fluorene	31.1	1.9	55.6	1.8	**1.8**
Phenanthrene	177.4	8.9	341.3	8.2	**1.9**
Anthracene	18.1	0.8	44.7	3.7	**2.5**
Fluoranthene	83.2	8.1	163.4	5.1	**2.0**
Pyrene	111.1	7.1	206.2	6.7	**1.9**
Benz[a]anthracene	7.1	1.4	12.1	0.6	**1.7**
Chrysene	11.8	1.6	23.1	1.1	**2.0**
Benzo[b + k] fluoranthene	4.7	0.6	8.4	0.4	**1.8**
Benzo[a]pyrene	3.5	0.7	4.4	0.3	**1.3**
Indeno[1,2,3-cd]pyrene	1.4	0.2	2.1	0.2	**1.5**
Benzo[ghi]perylene	6.1	0.4	11.4	0.6	**1.9**
Dibenz[ah]anthracene	ND	ND	0.6	0.1	*****
Mean	*37.8*	*3.5*	*65.0*	*2.9*	***1.8***

Table 2: PRC elimination constants (k_e) from passive samplers

PRC	1-PUF k_e (day^{-1})	2-PUF k_e (day^{-1})
PCB 14	0.035	0.037
PCB 21	0.014	0.013
PCB 30	0.036	0.036
PCB 204	0.006	0.005
d10 - Anthracene	0.036	0.034
d10 – Pyrene	0.006	0.007

Note: k_e calculated using equation [4]

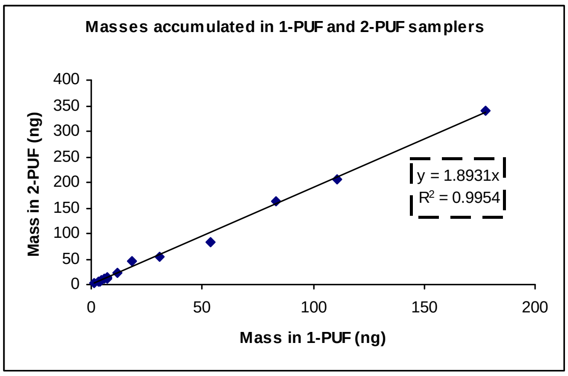

Figure 2: plot of PAH masses in both samplers

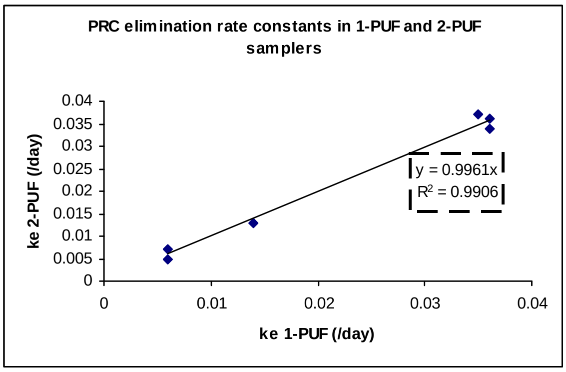

Figure 3: Plot of k_e values from both samplers

Figures 2 and 3 show these results graphically, with the accumulated masses and elimination rates from both samplers plotted against each other. These results will be used to assess the influence of the second PUF on uptake kinetics.

As can be seen from Table 1 all compounds sampled have accumulated in greater amounts into the 2-PUF samplers. An ideal scenario would be the accumulation of exactly double in the 2-PUF samplers, indicating that the samplers behave exactly as has been previously characterized for the 1-PUF samplers, and the two PUF disks are acting as one larger sampling phase. On average the ratio of masses in both samplers is 1.8 (masses 2-PUF/1-PUF) which is very close to the ideal. Slight deviations from this ideality do occur, but no discernible trend is seen toward intrinsic PAH properties such as molecular size or vapor pressure. The trend line in Figure 2 shows a slope close to the average factor difference of 1.8, which is very close to 2 ($R^2 = 0.99$).

If uptake kinetics had been influenced significantly by the presence of the second PUF disk, we would expect to see a difference in PRC elimination rate constants between the 1- and 2-PUF samplers. The initial results are positive in this regard; with both 1 & 2-PUF samplers showing virtually identical elimination rate constants (see Table 2 and Figure 3.). The trend line in Figure 3 has a slope of almost 1, indicating equivalent elimination rate constants from both samplers ($R^2 = 0.99$). From these results we can assume the kinetics of uptake in the 2-PUF samplers to be the same as that of the 1-PUF.

Conclusions

The new 2-PUF configuration of passive air sampler shows promise for collecting both particle and vapor phase PAHs with a greater efficiency than the traditional 1-PUF samplers used. Based on results from PRC elimination studies, and masses of PAHs accumulated, uptake kinetics for the 2-PUF samplers appears to be the same as previously characterized for 1-PUF samplers.

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